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Magnetic Nanocups

Hollow Spheres to Nanocups: Tuning the Morphology and Magnetic Properties of Single-Crystalline α-Fe_2O_3 Nanostructures**

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Dedicated to Professor C. N. R. Rao on the occasion of his 75th birthday

Futuristic technology to handle and manipulate reagents in very low volumes would certainly have immense impact on chemical and biological research. It is expected to find applications in enzyme kinetics studies,[1] immunoassays,[2] PCR analysis,[3] and all other fields where the quantity of the analyte is either extremely low or highly toxic to the environment. The synthesis of containers with nano- or zeptoliter volume has therefore become a cardinal step in developing such a technology. Mesoporous materials,[4] hollow capsules,[5] and nanotubes[6] are also envisaged to serve the intended purpose, but the synthesis of more complex morphologies, such as a bowl/cup, in large quantities is very challenging. Some attempts have been made in recent times to obtain micro- and nanobowls.[7–10] The reports by Xia et al.[11] on the synthesis of polymer hollow particles with controllable holes and by Gracias et al.[12] on obtaining self-folding metal submicrometer containers are noteworthy. Our research group recently reported the temperature-induced formation of ZnO zeptoliter bowls.[13]

The conventional approach to obtaining metal-oxide nanocups is based on the deposition of metal precursors on a self-assembled monolayer of colloidal spheres followed by their removal. However, the cups obtained in this method are polycrystalline or amorphous and the yield is limited to only the monolayer arrangement of spheres. Thus, a simple bottom-up approach, not restricted to monolayer assembly of colloidal spheres, is yet to be pursued. Herein, we report a new chemical strategy to tune the morphology of single-crystalline α-Fe_2O_3 from hollow spheres to nanocups by using carbonaceous spheres as templates. To our knowledge, this is the first method to obtain single-crystalline nanocups of a metal oxide. Interestingly, our observation seems to be against the well-documented approach of obtaining hollow spheres alone from such spherical templates.[14] The obtained nanostructures also show shape-dependent magnetic properties.

In a typical procedure, a suspension of carbon spheres in a solution of $Fe(NO_3)_3{\cdot}9H_2O$ in ethanol was stirred continuously at 35 to 38 °C until a thixotropic gel was obtained (see S1 of the Supporting Information). The formation of a gel is associated with the hydrolysis of ferric nitrate to iron oxohydroxide polymer.[15] Attaining the thixotropic gel before calcination was found to be mandatory to obtain hollow spheres and nanocups. Samples calcined before reaching the gel stage resulted in a porous α-Fe_2O_3 network.

The field-emission scanning electron microscopy (FESEM) image of α-Fe_2O_3 hollow spheres obtained by calcining the sample (with a gelation time of 12 h—see the Experimental Section) at 400 °C for 5 h shows a size variation from 100 to 400 nm (Figure 1 a), which is considerably smaller than the size of the carbon spheres (300–800 nm) used as the template. This shrinkage can be attributed to sintering and condensation of the metal oxide. The transmission electron

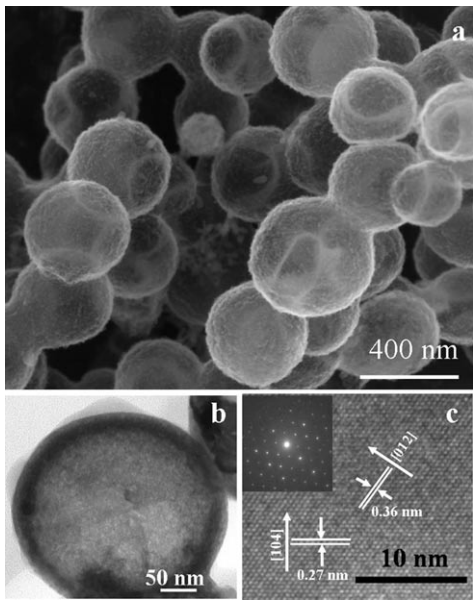

Figure 1. a) FESEM image of α-Fe_2O_3 hollow spheres. b) TEM image of an isolated hollow sphere. c) HREM image showing the lattice fringes of (012) and (104) planes. Inset: ED pattern obtained on a single sphere.

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microscopy (TEM) image in Figure 1b shows that the thickness of the wall of a hollow sphere is around 20 nm or less. The electron diffraction (ED) pattern (inset of Figure 1c) and the high-resolution electron microscopy (HREM) image further show that the spheres are single-crystalline (Figure 1c).

Figure 2a shows a low-magnification FESEM image of α-Fe_2O_3 nanocups of sizes ranging from 100 to 300 nm, in which the extent of shrinkage is higher than that of the hollow spheres. The nanocups were obtained by calcining the sample (gelation time 12 h) at 500 °C in air for 5 h. A double wall with folding along the rim of the cup was routinely observed in most of these cups (Figure 2b). Furthermore, the inward folding of these thin α-Fe_2O_3 walls at the rim of the cup can be clearly seen in the FESEM image at higher magnification (Figure 2c and S2 of the Supporting Information). The exposure of the underneath layer in the broken-up regions shows that the inner and outer walls of the cups may not be completely merged together (Figure 2b and c).

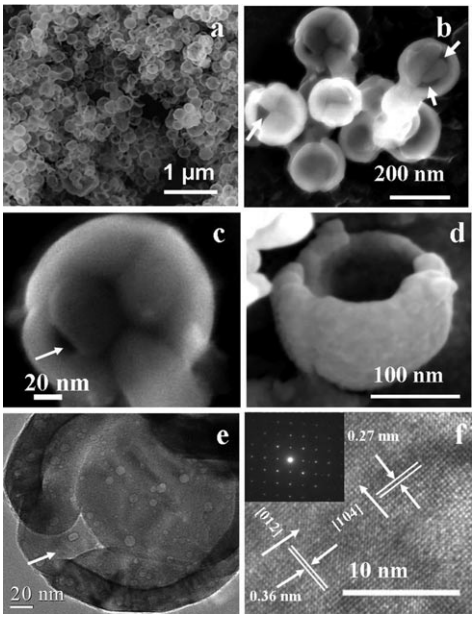

Figure 2. a) Low-magnification FESEM image of the α-Fe_2O_3 nanocups. b,c) Higher-magnification FESEM images of the cups showing the double-walled folding along the rim. White arrows indicate the broken-up regions. d) FESEM image of a single nanocup coated with gold. e) TEM image of a nanocup showing double-walled folding along the rim (white arrows). f) HREM image showing the lattice fringes of (012) and (104) planes. Inset: ED pattern of the nanocups.

A gold-coated cup with an improved contrast (Figure 2d) does not display the double wall as it is covered with the gold layer. The TEM image (Figure 2e) shows that the thickness of the double wall at the rim of a cup is about 20 nm. The transparent nature of these thin walls of size less than 10 nm is clearly seen at the fold. TEM α-tilting (from $+40°$ to $-40°$) analysis clearly distinguished the nanocups from hollow spheres by virtue of their prominent asymmetry along the rim created by the fold (see S3 of the Supporting Information). The HREM image (Figure 2f) and ED pattern (Figure 2f, inset) confirm the single-crystalline nature of these α-Fe_2O_3 nanocups, similar to that of the hollow spheres. The bottom of the cup is decorated with a lot of tiny pits whose contrast in the electron beam varies with depth (see S4 of the Supporting Information).

To understand the mechanism of cup formation, samples prepared with gelation times of 6, 12, and 20 h (the time required to reach the thixotropic gel) were calcined at different temperatures and their morphologies were examined. Thermogravimetric analysis (TGA) of the carbon spheres (separated from the thixotropic gels after thorough washing—see Experimental Section) shows that the iron content on the carbon spheres increases with an increase in gelation time (see S5A of the Supporting Information). TGA and the XRD pattern (see S5A and S6 of the Supporting Information) of the sample (gelation time 6 h) calcined at 250 °C for 5 h further indicate that the transformation of amorphous iron oxohydroxide to crystalline Fe_2O_3 begins well before the complete decomposition of the carbon spheres. Further calcination at 350 °C for 5 h removes 96% of the carbon and the spheres started to show buckling of the walls (Figure 3 and S5C of the Supporting Information). The thin walls of the spheres cannot withstand the stress caused by the crystallization and sintering of the iron oxide once the carbon spheres are decomposed. This stress is eventually relieved by buckling into controlled three-dimensional shapes.[16] If the sample is heated at 400 °C for 5 h, the buckling process completes as the top layer touches the bottom of the wall, which results in a cuplike morphology. Further, the exothermic heat generated by carbon combustion during folding may help to recrystallize (thermal annealing) the structures into single-crystalline cups.

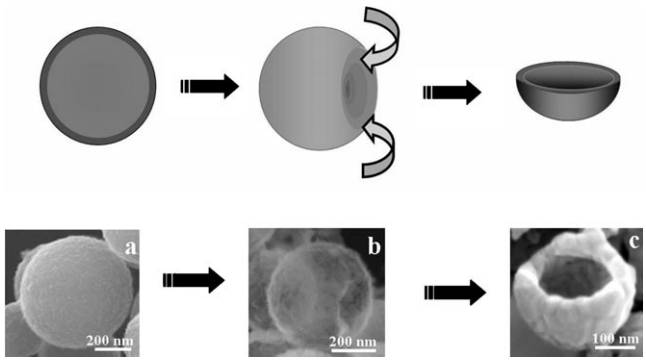

Figure 3. Top: temperature-induced shape evolution of α-Fe_2O_3 nanocups. Bottom: FESEM images of carbon spheres coated with gel (gelation time 6 h) and calcined at a) 250, b) 350, and c) 400 °C for 5 h (coated with gold).

On the other hand, the sample with relatively higher iron content prepared by increasing the gelation time to 12 h showed the cuplike morphology only when it was calcined at 500 °C for 5 h. The formation of hollow spheres on calcination at 400 °C suggests that the walls of the hollow spheres are thick enough to withstand the stress at that temperature. However, if the iron loading is too high (gelation time 20 h), the resulting morphology is always spherical irrespective of

calcination temperature (see S7 and S8 of the Supporting Information). Moreover, the resulting Fe_2O_3 spheres are polycrystalline and the wall thickness is around 40 nm. At higher loading, the local heat generated at the surface of the carbon spheres on calcination may not be felt evenly throughout the thick iron oxohydroxide coating, thus leading to smaller Fe_2O_3 crystals. This polycrystalline structure eventually helps to absorb the stress and blocks its propagation during carbon removal compared to single-crystalline Fe_2O_3. Increasing the ratio (wt/wt) of carbon spheres to ferric nitrate by three times gives a bowl-like morphology with a porous network on calcination at 500 °C (see S9 of the Supporting Information).

One-dimensional α-Fe_2O_3 nanorods, tubes, and wires by virtue of their shapes are known to show anisotropic magnetic properties compared to their spherical counterparts.[17] However, change in the magnetic properties with respect to a change in the three-dimensional complex morphology of single-crystalline α-Fe_2O_3, for example, from hollow sphere to nanocup, is not yet known. The bulk form of α-Fe_2O_3 is a canted antiferromagnet with a high Néel temperature of $T_N = 953$ K. At $T \approx 263$ K, it undergoes a Morin transition where there is a magnetic spin reorientation, below which the weak ferromagnetic component disappears.[18]

The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities (χ) of the α-Fe_2O_3 hollow spheres is shown in Figure 4a. This is typical of a superparamagnetic material with a blocking temperature of 100 K. The room-temperature magnetization data further confirm the superparamagnetic behavior of the hollow spheres (Figure 4b). Superparamagnetic properties are usually found in α-Fe_2O_3 particles of size less than 20 nm.[19] This property can therefore be attributed to the wall thickness of the single-crystalline hollow spheres, which is around 20 nm. Interestingly, it also shows a very weak transition at 200 K, probably because of the Morin transition associated with a very few buckling spheres that are at the beginning of transformation into cups.

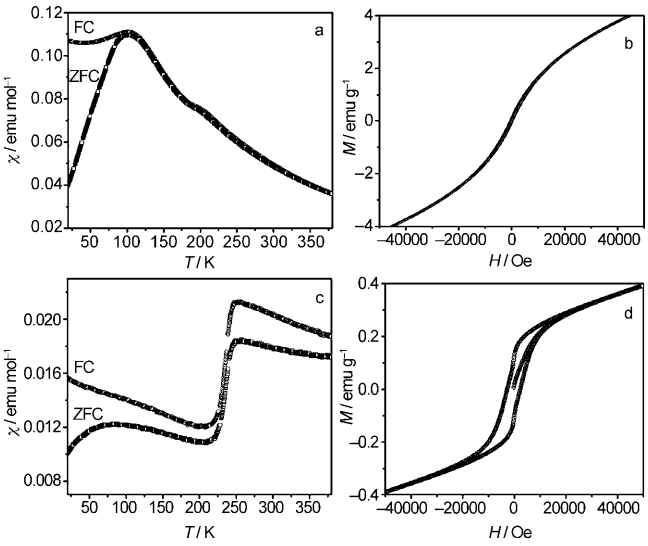

Figure 4. a,c) ZFC/FC (at 500 Oe) and b,d) *M*–*H* plots (at 300 K) of hollow spheres (a,b) and nanocups (c,d).

In sharp contrast to the superparamagnetic hollow spheres, nanocups with a wall thickness around 10 nm show bulk α-Fe_2O_3 behavior with a prominent Morin transition around 250 K (Figure 4c). Notably, a Morin transition is unlikely to be seen above 4 K if the particle sizes are in the range of 8 to 20 nm. Studies of crystalline, mesoporous α-Fe_2O_3 further revealed that walls of confined dimensions tend to suppress the Morin transition.[20] However, unlike the bulk, the irreversibility of the ZFC and FC magnetic susceptibilities below the Morin transition strongly suggest spin canting. The room-temperature magnetic moment–magnetic field (*M*–*H*) curve clearly confirms the canted antiferromagnetism in nanocups (Figure 4d). The shape anisotropy of the nanocups does indeed have a significant influence on their magnetic properties,[21] exhibiting a very high coercivity of 2587 Oe. To our knowledge this value is the highest among all the morphologies of α-Fe_2O_3 reported so far.[21]

In summary, we have reported a simple chemical route to synthesize single-crystalline α-Fe_2O_3 in the form of hollow spheres and nanocups. Interestingly, the magnetic properties result from the two-dimensional thin-filmlike walls of the three-dimensional nanostructures. The nanocups show a very large coercivity because of their complex shape anisotropy. It should also be possible to extend this procedure to obtain metal-oxide nanocups of those metal ions that can form oxohydroxide polymers under acidic or basic conditions.

Experimental Section

Synthesis of carbon spheres: Carbon spheres were synthesized by a previously reported method.[22] An aqueous solution of α-D-glucose (55 mL, 0.5 M) was placed in a 60-mL teflon-lined stainless steel autoclave. The solution was maintained at 180 °C for 16 h, after which it was allowed to cool naturally to room temperature. The solid brown product was collected by centrifuging at 10000 rpm for 5 min. It was thoroughly washed with ethanol and water and dried at 80 °C in air for 4 h.

Formation of thixotropic gel: In a typical synthesis, a suspension of carbon spheres (0.1 g) was prepared in a solution of $Fe(NO_3)_3 \cdot 9H_2O$ in absolute ethanol (10 mL, 0.5 M) by sonication in a water bath for 45 min. The suspension was magnetically stirred at 35 to 38 °C in a beaker to facilitate the gradual evaporation of ethanol. After a certain duration of continuous stirring under normal conditions (stirring time), the formation of the gel was induced by maintaining the relative humidity beyond 85% for 4–5 h. At this point, the gel possessed thixotropic properties. The total contact time of the carbon spheres in the ferric nitrate solution until it attained the gel state was taken as the gelation time and was adjusted to 6, 12, and 20 h by suitably accommodating both stirring time and gel induction time. The as-obtained carbon spheres coated with gel were washed thoroughly with water (Millipore) and ethanol and finally dried at 40 °C in air for 8 h. Calcination of the gel was performed at a suitable temperature to obtain the required morphology (see the Supporting Information).

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